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14. ABSTRACT The primary objective of this research is to make nanocomposites with the incorporation of thermally stable silicate nanolayers in the polymer matrix. Several functionalized imidazolium clays, functionalized anionic clays, and silylated apophyllites were synthesized and characterized by XRD and TGA. Thermal studies of functionalized clay have shown that the onset decomposition temperature of imidazolium functionalized clay (>325oC), alpha amino naphthonate exchanged layered double hydroxide (NLDH) (~300oC), and covalently silylated apophyllite (~420oC) can exceed the onset temperature of conventional organoclays (~260oC). Chemorheological measurements of 2 wt% organoclay filled epoxy have shown that the processing window is pretty wide after the addition of the organic layered-silicate to epoxy resin. The thermal stability of epoxy seems to be influenced by the addition of clay and diluent used in the epoxy system. In many cases, higher char yield for nanocomposites was observed suggesting clay is serving as catalyst and acting as barrier in the decomposition of the epoxy matrix. We also studied the thermal stability of tetra functional epoxy nanocomposite and a consistent small improvement in the onset temperature of the nanocomposite was noticed.					
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High Temperature Epoxy Nanocomposites for Aerospace Applications

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Project Summary

The field of clay filled polymer nanocomposite technology has gradually matured and many products using this technology have been commercialized. This is because significant improvement of the properties of the polymeric materials, including the mechanical, ablation, barrier, and flame retardancy, have been achieved with few wt% of clay addition. However, these improvements have been limited to low-temperature epoxy nanocomposites, and there have been very few reports for the high-temperature polymer layered-silicate nanocomposites with significant improvement of the properties. This is related to the thermal stability of the organic layered-silicate used in the nanocomposite. Although layered-silicate itself is stable after the loss of the water, the layered silicates are hydrophilic in nature and need to be organotreated so that they can be compatible with hydrophobic polymers. The organo-treatment of the layered-silicate is generally achieved through the ion-exchanged chemistry by the replacement of sodium cations with alkyl ammonium cations, which lowers the surface energy of silicate nanolayers and makes the layered silicate compatible with the polymer matrix. The interaction between the silicate backbone anion and ammonium cation is an ionic interaction and generally the cation decomposes from the layered silicate at $\sim 250^{\circ}\text{C}$. Thus, the primary objective of this research is to make the high-performance nanocomposite materials with the incorporation of thermally stable silicate nanolayers in the polymer matrix. Some of the thermally stable clays synthesized and characterized in this study are the cation exchanged montmorillonite, anion exchanged layered double hydroxide (LDH) and silylated apophyllite. At HU, we used imidazolium salt as substitutes for the conventional alkyl ammonium surfactant towards functionalizing MMT clay and 6 amino 2 naphthanoic acid as substitutes towards functionalizing magnesium layered double hydroxide. At UDRI, several functionalized apophyllites were synthesized and characterized by a number of analytical techniques. Thermal studies of synthesized functionalized clay have shown that the onset decomposition temperature of imidazolium functionalized clay ($\geq 325^{\circ}\text{C}$), alpha amino naphthononate exchanged layered double hydroxide (NLDH) ($\sim 300^{\circ}\text{C}$), and covalently silylated apophyllite ($\sim 420^{\circ}\text{C}$) can exceed the onset temperature of conventional organoclays ($\sim 260^{\circ}\text{C}$). Chemorheological measurements of 2 wt% organoclay filled epoxy have shown that the processing window

is pretty wide after the addition of the organic layered-silicate with high thermal stability. The thermal stability of epoxy seems to be influenced by the addition of clay and diluent in the epoxy system. In many cases, higher char yield for nanocomposites was observed suggesting clay is serving as a catalyst and acting as a barrier in the decomposition of the epoxy matrix. Occasionally, we noticed lower char yield which seems to suggest that the sample is heterogeneous with some of the intercalant in the clay platelets influencing the char yield of nanocomposite. We also investigated the thermal stability of technologically more relevant high T_g epoxy resin (tetra functional epoxy) nanocomposite. A consistent small improvement in the onset temperature of the high performance nanocomposite was noticed.

HU Research Summary:

Ionic liquids can be used instead of alkyl ammonium salt to improve the thermal stability and flame retardancy of nanocomposites. The cations in the clay gallery can be exchanged by imidazolium based ions using a standard ion exchange technique, with a procedure similar to the one used for the alkyl ammonium ions. In this work, we assessed the potential of using alkyl imidazolium salts in functionalizing clays for use in formulation of high performance epoxy nanocomposite. We synthesized homologous series of hydroxyl-substituted imidazolium salts by initially reacting 2-methylimidazole with sodium hydride and bromohexadecane to form 1-hexadecyl-2-methyl imidazole. The compound was either protonated to form 1-hexadecyl-2-methylimidazolium chloride (HDMIM.HCl) or was reacted with appropriate chloroalcohols in anhydrous acetonitrile to yield 1-hexadecyl-3-(10-hydroxydecyl)-2-methylimidazolium chloride (HDMIM), 1-hexadecyl-3-(6-hydroxyhexyl)-2-methylimidazolium chloride (HHMIM), and 1-hexadecyl-3-(2-hydroxyethyl)-2-methylimidazolium chloride (HEMIM). The synthesized compound(s) were characterized by ^1H NMR, 2D NMR, and matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Figure 1 is the representative ^1H NMR and MALDI-TOFMS of HDMIM.HCl. The onset decomposition temperature (T_d), defined as the temperature at which 5 % mass loss occurs, was recorded for all the imidazolium functionalized clay (Table 1) and was found to be ≥ 325 °C. The widely used alkyl ammonium salts have a lower onset decomposition temperature (e.g., 267 °C for AA-MMT). The improved stability of imidazolium-

functionalized clay can be attributed to the delocalization of cation and the rigidity of the imidazolium ring. Isothermal TGA measurements at 200 °C in nitrogen atmosphere for HH-MMT and AA-MMT confirm the higher thermal stability of imidazolium functionalized clay as compared to quaternary ammonium modified clays (Figure 2). Based on the extrapolated data of the weight vs. time curve, the asymptotic value of mass loss is below 3 % for HH-MMT and above 6 % for AA-MMT. Because of higher thermal stability, imidazolium functionalized clay can be used in formulating high-temperature clay filled matrix materials such as bismaleimide, polyimide, and high-functional-epoxy resin. These imidazolium modified clay filled matrix can be especially useful in the formulation of fiber reinforced composites for aerospace and automobile applications that require high operating temperatures.

The research efforts also focused on synthesizing layered material with appropriate organic modifiers. The alpha amino naphthonate exchanged layered double hydroxide (NLDH) was prepared by co-precipitating a solution of Mg^{2+} and Al^{3+} nitrate with NaOH, then adding the deprotonated form of 6 amino 2 naphthoic acid (deprotonated with NaOH). It takes 6 moles of OH^- , per Al^{3+} , for the synthesized LDH. The suspension was stirred and refluxed at 100°C for 1 day, under a nitrogen gas blanket. The synthesis of NLDH was performed by NIST scientist and has been used as nanofiller in the formulation of nanocomposite. NLDH was selected because it has amino pendant group and it can improve the compatibility between the layered double hydroxide and epoxy. The FTIR spectrum shows characteristic peak for carbonate anion in LDH and aromatic in plane bending & aromatic C=C stretching peaks in NLDH. Also the FTIR spectrum of NLDH shows an intense and broad peak at 3376 cm^{-1} belonging to N-H/O-H stretching indicating that amine functional groups is introduced into the layered double hydroxide. WAXD results of NLDH show an increase in the d-spacing (d_{003}) from 0.75 nm to 1.75 nm suggesting that organic carboxylate anion has been successfully intercalated in LDH gallery. TGA results of NLDH (Figure 3) show a three-step decomposition profile with peaks identified to loss of interlayer water, dehydroxylation, and decomposition of the organic anion from NLDH. The decomposition of organic anion from NLDH was found to occur at $\sim 305^\circ\text{C}$, which is much higher than that has been reported for general organoclays ($\sim 267^\circ\text{C}$ for AA-MMT). Our results indicate that

NLDH has far superior thermal stability than the general organoclays. The enhancement in the thermal stability of NLDH organoclay over the conventional organoclay can be attributed to aromatic ring structure presence in the NLDH organoclay.

Initially, epoxy-clay nanocomposites were prepared by dispersing imidazolium-modified clays in diglycidyl ether of bisphenol A (DGEBA) mixture by performing sonication with glycidyl methacrylate (GMA) as a swelling agent and meta phenylene diamine (m-PDA) as a curing agent. X-ray diffraction (XRD), laser scanning confocal microscopy (LSCM), and transmission electron microscopy (TEM) of the 3.5 % organoclay filled epoxy nanocomposites show that sonicated samples have a more homogeneous clay distribution and smaller aggregate size of intercalated clay tactoids, as compared to the hand mixed samples. Torsional dynamical mechanical analysis (TDMA) data shows a general increase in the storage modulus of the sonicated nanocomposites and a decrease in the glass transition temperature as compared to the pristine epoxy resin (Figure 4). The non-uniformly dispersed clay filler promotes heterogeneous regions of lightly crosslinked regions which lowers the thermal stability of nanocomposite.

Additionally, the dispersion of imidazolium clay in difunctional epoxy resin (DER 661) and tetraglycidyl ether diamino diphenyl methane (TGDDM) was investigated by high shear mixing the swollen mixture at 60°C at 250 rpm for 15 minutes. The morphology of diphenyl dimethane sulfone cured epoxy specimen was characterized by XRD, TEM, and LSCM. LSCM shows good dispersion of imidazolium functionalized clay in the epoxy matrix. TEM micrographs of epoxy nanocomposite show that there are about 3-5 clay sheets and occasionally more clay sheets present in a stack. The observed morphology can at best be described as intercalated. The onset decomposition temperature for the functionalized nanocomposite was approximately 15°C greater than Cloisite 30B nanocomposite. Isothermal TGA measurements of nanocomposites and epoxy specimen under nitrogen atmosphere at 200°C show an initial phase (where a sharp drop in mass is noticed) and a second phase that is accompanied by a gradual drop in mass. The extent of decline in the mass of the second phase was found to be sensitive to the nanofiller used in the formulation of the nanocomposite. For example, Cloisite 30B nanocomposite was more susceptible to mass loss while imidazolium functionalized nanocomposite was less susceptible to mass loss.

We also investigated the thermal stability of NLDH filled epoxy nanocomposites. Initially, the functionalized anionic clay was vigorously mixed for 2h with difunctional epoxy resin (DGEBA) that contained small fraction of reactive diluent 1,4 butanediol glycidyl ether, followed by curing with mctaphenylene diamine for 3h at 65°C and 2h at 125°C. The cure chemistry of epoxy with and without addition of functionalized layered double hydroxide was followed by recording the intensity of the IR peak at 915 cm⁻¹, corresponding to the oxirane group using FTIR. The functionalized layered double hydroxide did not significantly impact the epoxy crosslink chemistry, as evidenced by the consumption of oxirane rings. WAXD results of 2 wt% and 5 wt% NLDH epoxy nanocomposite showed a broad diffused peak that may be from the ordered stacks of layered material in the nanocomposite. Visual inspection of the nanocomposite showed higher transparency of the sample compared to the conventional hand mixed nanocomposite. TEM of NLDH epoxy nanocomposite showed random dispersion of stacked lamellar structure with several sheets present in the stack. The observed morphology can at best be described as intercalated.

We noticed a significant increase in the onset decomposition temperature of the difunctional epoxy resin that contained small fraction of reactive diluent 1,4 butanediol glycidyl with the addition of NLDH nanofillers. Regardless of the definition used in describing the onset decomposition temperature (5% mass loss or 10% mass loss), we consistently noticed a higher thermal stability for nanocomposite. The enhancement in thermal stability of the nanocomposite was noticed for all filler composition and a greater enhancement in the thermal oxidative stability was observed at higher anionic clay loading. For example, the decomposition temperature $T_{dec \text{ at } 5\%}$ of the epoxy resin under air atmosphere was found to increase by 25°C upon 2 wt% NLDH addition and increase by 30°C upon addition of 5 wt% NLDH. Additionally, we noticed heating rate to impact the onset decomposition of the resin and nanocomposite. For example, the onset decomposition temperature in the neat DGEBA resin to increase from ~300°C to ~330°C in the 2 wt% NLDH nanocomposite at 10°C/min heating rate, while it increases from ~305°C in the neat DGEBA resin to ~340°C in the 5 wt% NLDH nanocomposite at 20°C/min heating rate.

In the next phase of the research, an attempt was made to replicate the success achieved in improving the thermal stability of the difunctional epoxy resin upon addition of NLDH to tetrafunctional epoxy nanocomposite system. NLDH was smear mixed with hot tetradiglycidyl diaminodiphenyl methane (TGDDM) for 3h and the mixture was stirred at 250 rpm in a bath maintained at 100°C for 1h. The mixture was further stirred for an additional 15 minutes in a bath maintained at 130°C upon addition of 4,4'-diaminodiphenylsulfone (DDS). The mixture was cured for 3h at 130°C, 2h at 150°C and 2h at 180°C. The intensity of the IR peak at 902 cm^{-1} , corresponding to the oxirane group was used to identify the ring-opening reaction. The intensity of the oxirane ring IR peak in cured resin and nanocomposite was found to be nearly similar suggesting that epoxy resin crosslink chemistry is not much affected upon the addition of 2 wt% NLDH. Confocal microscopy shows good dispersion of anionic clay near the surface and considerable aggregation of layered double hydroxide in the bulk. WAXD results of nanocomposite show a broad diffused peak that may be from the aggregates of layered material in the nanocomposite.

Thermal stability measurements of epoxy nanocomposites showed an improvement in the onset decomposition temperature of the TGDDM upon addition of NLDH. Similarly, improvements in thermo-oxidative stability measurements of nanocomposite were noted. Regardless of the heating rate used in the TGA measurement of the nanocomposite, there was a minimum 10°C improvement in the onset decomposition temperature of the epoxy resin upon addition of 2wt% NLDH. Additionally, we noticed the main endothermic peak for nanocomposite to appear at an elevated temperature. The appearance of main endothermic peak at elevated temperature is encouraging and is useful in improving the flame retardancy of the resin. The reason for the less than desired improvement in the onset decomposition temperature of tetrafunctional epoxy resin nanocomposite compared to difunctional epoxy nanocomposite is not clear. This is perhaps due to the poor dispersion of the layered sheets in tetrafunctional epoxy. We have shown that the onset temperature of difunctional epoxy (DGEBA) system and tetrafunctional epoxy (TGDDM) system can be increased by ~35°C and ~10°C, respectively upon the addition of few wt% of NLDH to the pristine resin.

UDRI Research Summary:

Several functionalized apophyllites (octyldimethylsiloxy grafted apophyllite, 7-octenyldimethylsiloxy grafted apophyllite, cyanopropyldimethylsiloxy grafted apophyllite, aminopropyldimethylsiloxy grafted apophyllite, and isocyanopropyldimethylchlorosilane grafted apophyllite) were synthesized and characterized by FTIR, XRD and TGA. The functional group was introduced to the apophyllite so as to improve the compatibility between the organic layered-silicate and polymer matrix.

Initially, three different *n*-octyldimethylsiloxy-apophyllites with different organic-grafting degrees were prepared through the control of the ratio of the reactants and characterized through the wide-angle x-ray diffraction. The WAXD and TGA studies show that original cations in the *n*-octyldimethylsiloxy-apophyllite have been replaced by the proton and silylation is good. However, the extent of grafting in silylated apophyllite (A-OMM #2201 and A-OMM #2202) is different. The substitution level of the grafted organic siloxy group in A-OMM (#2202) is higher than that of A-OMM (#2201). The decomposition temperature of the A-OMM (#2201) and A-OMM (#2202) are very high (~435°C for #2201, and ~415°C for #2202). However, the decomposition temperature of traditional organoclays such as I.30E and Cloisite 30B is ~250°C, which is ~160°C less than that of A-OMM (#2202) (refer to Figure 5). The reason for so large difference of the decomposition temperature is due to the fact that the interaction between the organic pendant group and silicate sheet backbone in Cloisite 30B or I.30E is ionic while that in A-OMM (#2202) is strong siloxy covalent bonding.

The introduction of the C=C group (e.g. the 7-octenyldimethylsiloxy group) in the grafted organic-apophyllite was also successful. Fourier transform infrared (FTIR) spectroscopy, wide-angle x-ray diffraction (WAXD) (refer to Figure 6), and thermal gravimetric analysis (TGA) characterization results of the modified silicates indicate that the organic pendant group has been chemically grafted on to the backbone of layered material and the organically modified layered material is thermally stable up to ~400°C, much higher than the general organoclays (~250°C). C=C group is active functional group and can be used as precursor for other functional group such as hydroxyl group, amino group, which can have direct organic covalent bonding with epoxy resin.

Additionally, polar cyano ($\text{C}\equiv\text{N}$) group was introduced in the organic layered-silicate. The cyanopropyldimethylsiloxyl group was successfully grafted on the backbone of the silicate nanosheets. The FTIR spectrum indicates that organic group including $\text{C}\equiv\text{N}$ (2246 cm^{-1}) was inside the organic layered-silicate. The x-ray diffraction shows the gallery height was increased to 17.7 \AA , which further confirms that the organic group is intercalated inside the gallery (nanoconfinement environment) rather than just on the surface of the particle. The TGA data shows that the decomposition temperature for this A-CMM is very high ($\sim 445^\circ\text{C}$), which indicates the strong covalent bonding between the organic group and silicate sheet backbone rather than just intermolecular interaction. The cyano group is very polar ligand and this A-CMM was found to be very well compatible with thermosetting materials and the interfacial interaction (polar-polar) will be stronger than the molecular interaction of non-polar with polar.

Next, we addressed the processing issue to making the high-performance composite. The DSC studies of the systems (MY720-DER663-DDS) with and without organo layered silicate showed that both systems behave very similarly, indicating the incorporation of octyldimethylsiloxyl grafted apophyllite (A-OMM) does not change much the cure chemistry of the epoxy. The rheology test was run via the viscosity between parallel plates and it showed that the trend of the viscosity curve with and without A-OMM is similar. The viscosity of A-OMM-Epoxy mixture was increased to ~ 30 poise at 170°C after 35 min. (ramp test, $2^\circ\text{C}/\text{min}$, the initial temperature is 100°C); while the complex viscosity of pure epoxy was increased to ~ 30 poise at $\sim 190^\circ\text{C}$ in 45 minutes (refer to Figure 7). This indicates that the processing windows of both cure cycle or ramp cure are still pretty wide after the addition of the type of organic layered-silicate with highly-thermal stability.

Finally, nanocomposites were prepared by mixing 3-cyanopropyldimethylsiloxyl-apophyllite with Epon 862 in the presence of acetone using ultrasonicator. The cyano group is very polar ligand and the organic layered-silicate was found to be compatible with epoxy resin (containing polar $-\text{OH}$ group) and the interfacial interaction (polar-polar) was stronger than the weak molecular interaction between non-polar alkyl chain of ammonium modified clay and polar group of epoxy resin. This was confirmed by the X-ray diffraction data of the mixture of 3-cyanopropyldimethylsiloxyl-apophyllite with Epon

862. There was no peak at low 2θ angle region for the mixture and thus this organic layered-silicate was exfoliated in the Epon 862. In addition, the X-ray diffraction data of the cured sample of the 3-cyanopropyldimethylsiloxylapophyllite with Epon 862 and curing agent showed no peak at low 2θ angle region, indicating an exfoliated nanostructure.

The thermal stability of the epoxy nanocomposite with 1.7 wt. % 3-cyanopropyldimethylsiloxylapophyllite loading showed some improvement. The decomposition temperature of the nanocomposite is 374°C vs. 364°C for pure epoxy ($10^{\circ}\text{C}/\text{min}$, under nitrogen), while the char yield of the nanocomposite is 17% vs. 11% for pure epoxy. The higher loading of the organic layered-silicate such as 5wt% should improve further the thermal stability of the nanocomposite. To our knowledge, this is the first report for the epoxy nanocomposite containing the cyano group functionalized silylated silicate with higher-thermal stability.

The high thermal stability of the synthesized organic layered-silicate does not translate to significant improvement in the onset decomposition temperature of high-temperature epoxy nanocomposite since the curing temperature for high-temperature epoxy is $\sim 180^{\circ}\text{C}$, which the traditional organoclay can still stand. However, for the aerospace relevant polyimide system, the traditional organoclay, even the imidazolium-montmorillonite may not stand the curing temperature of 370°C of the aerospace polyimide resin. In these systems, the new organic layered-silicate with high thermal stability ($\sim 430^{\circ}\text{C}$) can be used for formulation of next generation aerospace nanocomposite matrix materials.

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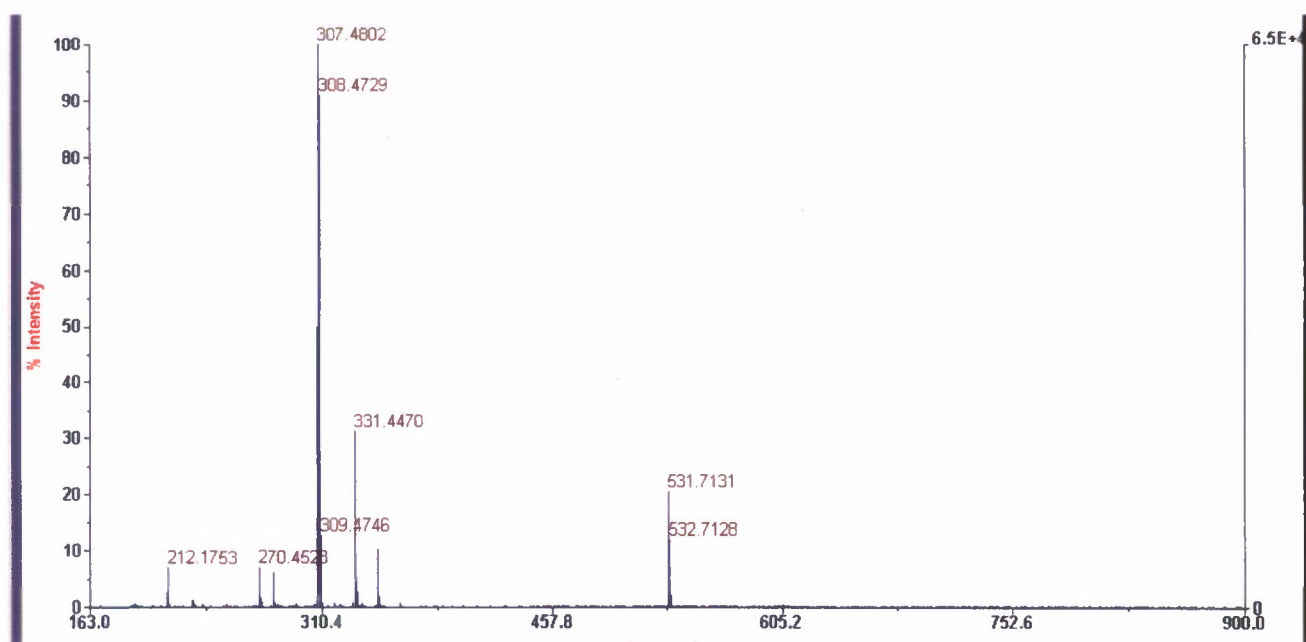
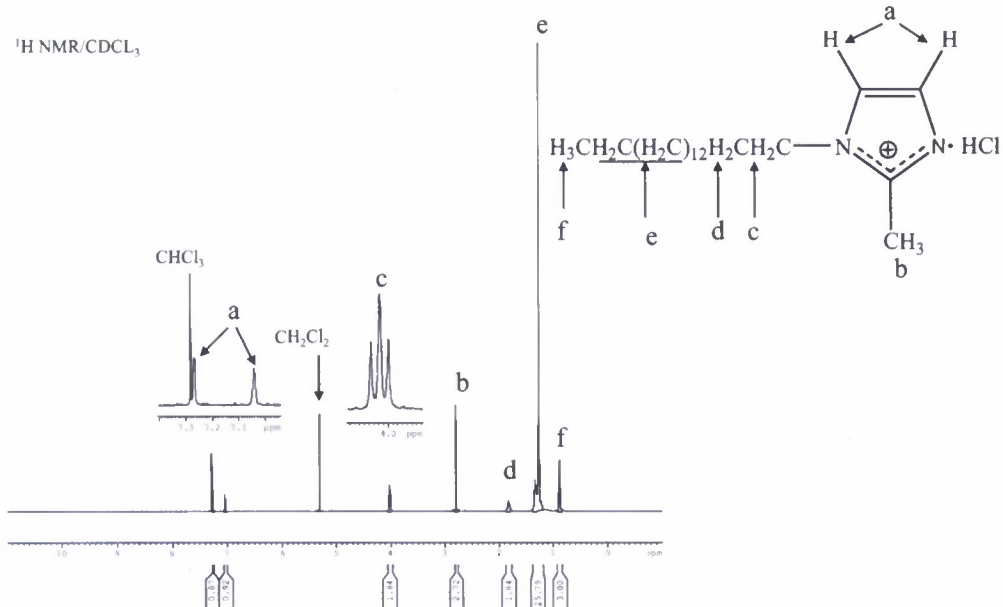


Figure 1: ^1H NMR spectrum of protonated 1-hexadecyl-2-methylimidazolium hydrochloride (HDMIM.HCl)